



Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2369137 A1 2000/10/19

(21) 2 369 137

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 2000/03/27
(87) Date publication PCT/PCT Publication Date: 2000/10/19
(85) Entrée phase nationale/National Entry: 2001/10/09
(86) N° demande PCT/PCT Application No.: EP 2000/002666
(87) N° publication PCT/PCT Publication No.: 2000/061370
(30) Priorités/Priorities: 1999/04/09 (199 16 141.0) DE;
1999/09/10 (199 43 545.6) DE

(51) Cl.Int.⁷/Int.Cl.⁷ B32B 27/32, B65D 65/40, B29C 45/16,
B29C 45/00, B29C 45/14, C08G 61/08

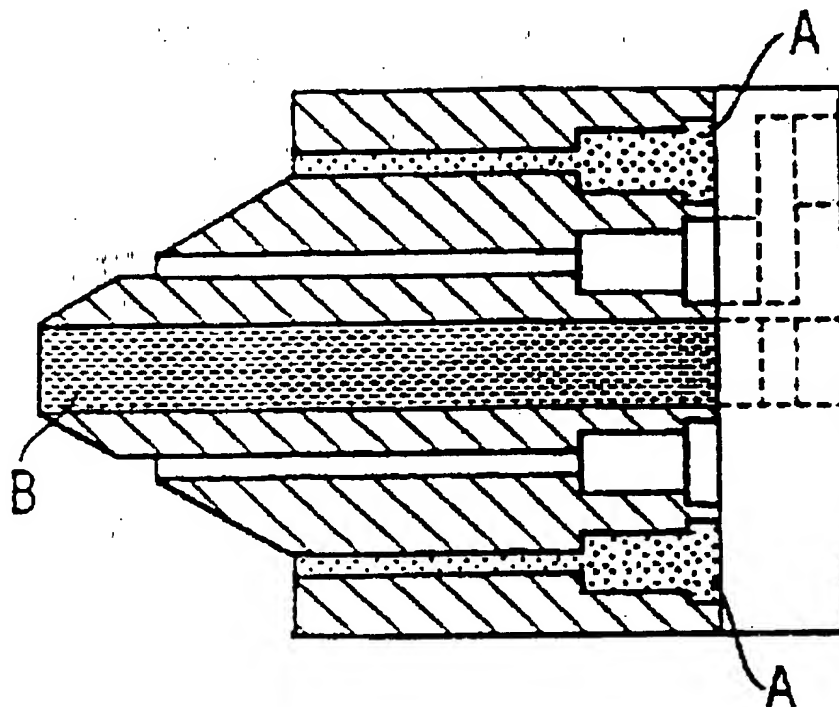
(71) Demandeur/Applicant:
TICONA GMBH, DE

(72) Inventeurs/Inventors:
SULLIVAN, VINCENT, US;
SCHULZ, DETLEF, DE;
JACOBS, ALEXANDRA, DE

(74) Agent: BERESKIN & PARR

(54) Titre : CONTENANTS MULTICOUCHES AYANT UNE ADHERENCE AMELIOREE ENTRE LES COUCHES
POLYMERIQUES ET D'EXCELLENTE PROPRIETES BARRIERE

(54) Title: MULTILAYER CONTAINERS EXHIBITING AN IMPROVED ADHERENCE BETWEEN POLYMER LAYERS AS
WELL AS EXCELLENT BARRIER CHARACTERISTICS



(57) Abrégé/Abstract:

The invention relates to multilayer containers containing at least one cycloolefin polymer, to a method for producing these multilayer containers, and to the use of the inventive multilayer containers.

1999/G008/WO

Abstract

Multilayer containers having improved adhesion between the polymer layers and excellent barrier properties

The present invention relates to multilayer containers comprising at least one cycloolefin polymer, to a process for producing these multilayer containers and to the use of these multilayer containers.

WO 00/61370

PCT/EP00/02666

Description

Multilayer containers having improved adhesion between the polymer layers and excellent barrier properties

5

The present invention relates to multilayer containers comprising at least one cycloolefin polymer, to a process for producing these multilayer containers and to the use of these multilayer containers.

10

JP-A-4 276 253 discloses multilayer containers comprising a layer of a thermoplastic saturated norbornene polymer which has been prepared by ring-opening metathesis polymerization and a further layer of a thermoplastic polymer having good gas barrier properties.

15

JP-A-9 239 909, JP-A-7 171 858 and JP-A-9 011 416 disclose polyolefin/polycycloolefin multilayer containers which are suitable for the packaging of foods due to a further layer of a thermoplastic polymer having good oxygen barrier properties. The use of a bonding layer which improves adhesion between the different polymer layers is also described.

20

EP-A-824 067 and JP-A-10 059 343 likewise describe multilayer containers which are made up of polyolefin layers and polycycloolefin layers and are able to keep in flavors and are thus suitable, for example, for the packaging and storage of toothpaste. In these patent publications, it is stated that the

25

layers of various polymers are joined by means of bonding layers.

It is an object of the present invention to provide multilayer containers having improved adhesion between the layers and also an economical and environmentally friendly process for producing multilayer containers. For

30

the purposes of the present invention, multilayer containers are containers which are made up of two or more layers of polymers.

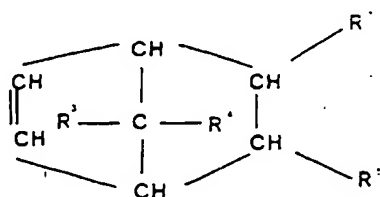
35

The object of the present invention is achieved by multilayer containers comprising suitable cycloolefin polymers.

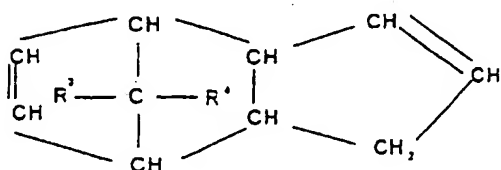
The multilayer containers of the invention comprise at least one cycloolefin polymer which comprises polymerized units derived from at least one cyclic, in particular polycyclic, olefin and, if desired, from at least one

acyclic olefin. The term cycloolefin polymer encompasses cycloolefin copolymers as well as cycloolefin homopolymers.

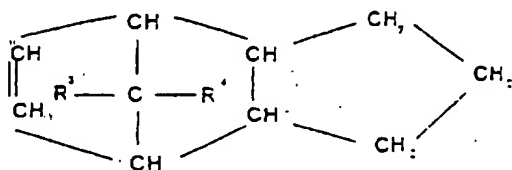
- 5 The multilayer containers of the invention comprise two or more polymer layers of which at least one polymer layer comprises at least one cycloolefin polymer comprising from 0.1 to 100% by weight, preferably from 0.1 to 99.9% by weight, particularly preferably from 3 to 75 mol%, based on the total mass of the cycloolefin polymer, of polymerized units derived from at least one polycyclic olefin of the formulae I, II, II', III, IV, V or VI



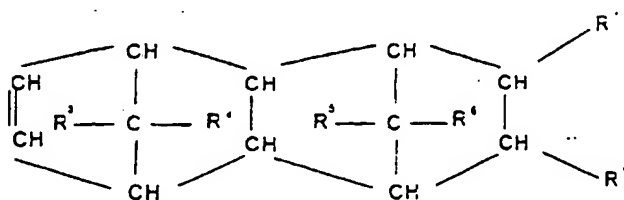
(I),



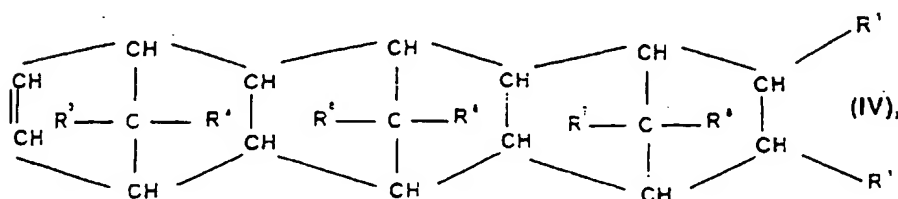
(II),



(II'),

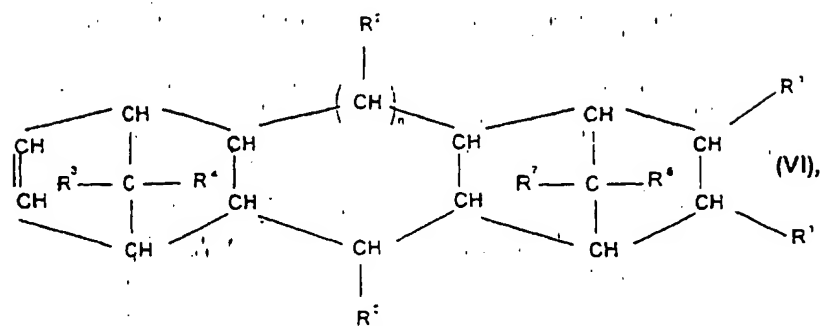
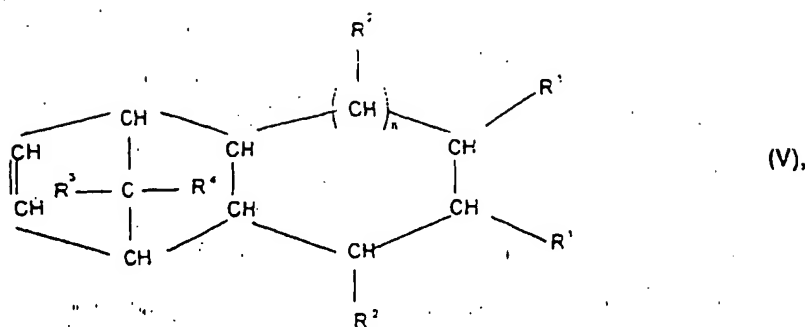


(III),

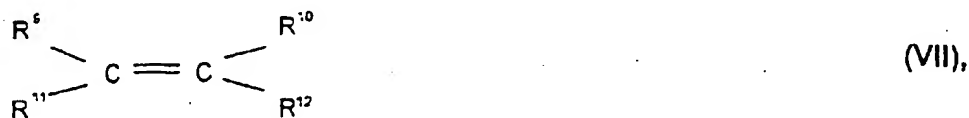


(IV),

3



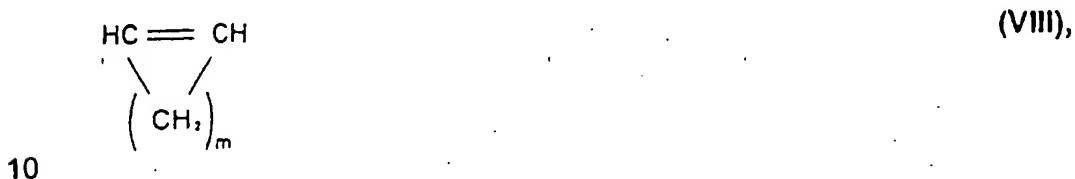
- where $R^1, R^2, R^3, R^4, R^5, R^6, R^7$ and R^8 are identical or different and are each a hydrogen atom or a C_1 - C_{20} -hydrocarbon radical such as a linear or branched C_1 - C_8 -alkyl radical, C_6 - C_{18} -aryl radical, C_7 - C_{20} -alkylenaryl radical, a cyclic or acyclic C_2 - C_{20} -alkenyl radical or form a saturated, unsaturated or aromatic ring, where identical radicals R^1 to R^8 in the various formulae I to VI may have different meanings and n is from 0 to 5, and from 0 to 99.9% by weight, preferably from 0.1 to 99.9% by weight, particularly preferably from 5 to 80 mol%, based on the total mass of the cycloolefin polymer, of polymerized units derived from one or more acyclic olefins of the formula VII



- where R^9, R^{10}, R^{11} and R^{12} are identical or different and are each a hydrogen atom or a linear, branched, saturated or unsaturated C_1 - C_{20} -hydrocarbon radical such as a C_1 - C_8 -alkyl radical or a C_6 - C_{18} -aryl radical.

The cyclic olefins also include derivatives of these cyclic olefins containing polar groups such as halogen, hydroxyl, ester, alkoxy, carboxy, cyano, amido, imido or silyl groups.

- 5 In addition, the cycloolefin polymers used according to the invention for microstructured components can further comprise from 0 to 45% by weight, based on the total mass of the cycloolefin polymer, of polymerized units derived from one or more monocyclic olefins of the formula VIII



where m is from 2 to 10.

- 15 For the purposes of the present invention, preference is given to cycloolefin polymers which comprise polymerized units derived from polycyclic olefins of the formula I or III and polymerized units derived from acyclic olefins of the formula VII.

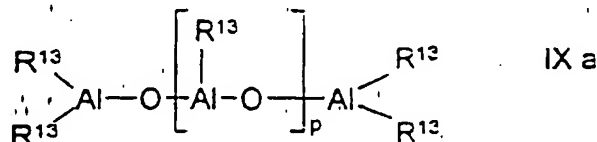
- 20 Particular preference is given to cycloolefin polymers which comprise polymerized units derived from olefins having a norbornene skeleton, very particularly preferably from norbornene and tetracyclododecene and, if desired, vinylnorbornene or norbornadiene. Particular preference is also given to cycloolefin polymers which comprise polymerized units derived from acyclic olefins having terminal double bonds, e.g. α -olefins having
- 25 from 2 to 20 carbon atoms, very particularly ethylene or propylene. Exceptional preference is given to norbornene-ethylene and tetracyclododecene-ethylene copolymers.

- 30 The preparation of the cycloolefin polymers can be carried out by means of heterogeneous or homogeneous catalysis by organometallic compounds, as described in many patents.

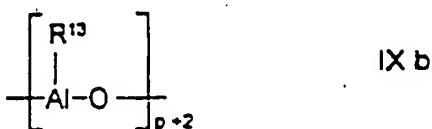
- 35 The cycloolefin polymers used according to the invention can be prepared at temperatures of from -78 to 200°C and a pressure of from 0.01 to 200 bar in the presence of one or more catalyst systems which comprise at least one transition metal compound and, if appropriate, a cocatalyst and, if

appropriate, a support material. Suitable transition metal compounds are metallocenes, in particular stereorigid metallocenes. Examples of catalyst systems which are suitable for the preparation of the cycloolefin polymers used according to the invention are described in EP-A-407 870, EP-A-485 893 and EP-A-503 422. These references are hereby expressly incorporated by reference.

The cycloolefin polymers used according to the invention can be prepared using a metallocene as transition metal compound and an aluminoxane of the formula IXa

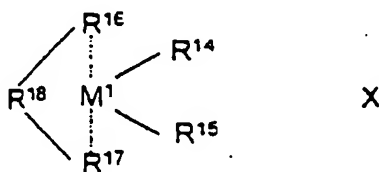


for the linear type and/or the formula IXb



for the cyclic type, where, in the formulae IXa and IXb, R^{13} is a C_1 - C_6 -alkyl group or phenyl or benzyl and p is an integer from 2 to 50.

The transition metal component can be a metallocene of the formula X

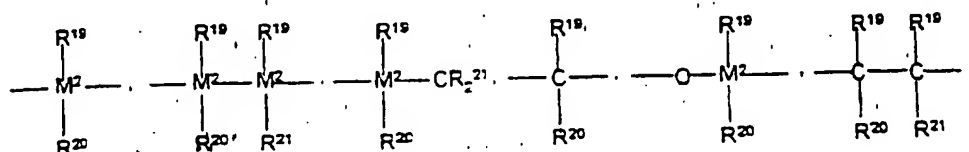


where
 M^1 is a metal of groups 3 to 10 or the lanthanide series of the Periodic Table of the Elements, preferably titanium, zirconium, hafnium, vanadium,

niobium or tantalum,

R^{14} and R^{15} are identical or different and are each a hydrogen atom, a halogen atom, a C₁-C₁₀-alkyl group, a C₁-C₁₀-alkoxy group, a C₆-C₁₀-aryl group, a C₆-C₁₀-aryloxy group, a C₂-C₁₀-alkenyl group, a C₇-C₄₀-arylalkyl group, a C₇-C₄₀-alkylaryl group or a C₈-C₄₀-arylalkenyl group,

R^{16} and R^{17} are identical or different and are each a monocyclic or polycyclic hydrocarbon radical which can form a sandwich structure, with the central atom M^1 ,



$= BR^{19}$, AlR^{19} , $-Ge-$, $-Sn-$, $-O-$, $-S-$, SO_2 , NR^{19} , CO , PR^{19} or $P(O)R^{19}$, where R^{19} , R^{20} and R^{21} are identical or different and are each a hydrogen

atom, a halogen atom, a C₁-C₁₀-alkyl group, a C₁-C₁₀-fluoroalkyl group, a C₆-C₁₀-fluoroaryl group, a C₆-C₁₀-aryl group, a C₆-C₁₀-aryloxy group, a C₁-C₁₀-alkoxy group, a C₂-C₁₀-alkenyl group, a C₈-C₄₀-arylalkyl group, a C₇-C₄₀-alkylaryl group or a C₈-C₄₀-arylalkenyl group or R^{19} , R^{20} and R^{21} in each case together with the atoms connecting them form a ring, and

M^2 is silicon, germanium or tin.

Examples of transition metal compounds used are:

- rac-dimethylsilylbis(1-indenyl)zirconium dichloride,
- rac-dimethylgermylbis(1-indenyl)zirconium dichloride,
- rac-phenylmethylsilylbis(1-indenyl)zirconium dichloride,
- rac-phenylvinylsilylbis(1-indenyl)zirconium dichloride,
- 1-silacyclobutylbis(1-indenyl)zirconium dichloride,
- rac-diphenylsilylbis(1-indenyl)hafnium dichloride,
- rac-phenylmethylsilylbis(1-indenyl)hafnium dichloride,
- rac-diphenylsilylbis(1-indenyl)zirconium dichloride,
- rac-ethylene-1,2-bis(1-indenyl)zirconium dichloride,
- dimethylsilyl(9-fluorenyl)(cyclopentadienyl)zirconium dichloride,
- diphenylsilyl(9-fluorenyl)(cyclopentadienyl)zirconium dichloride,
- bis(1-indenyl)zirconium dichloride,
- diphenylmethylene(9-fluorenyl)cyclopentadienylzirconium dichloride,

- isopropylene(9-fluorenyl)cyclopentadienylzirconium dichloride,
 rac-isopropylidenebis(1-indenyl)zirconium dichloride,
 phenylmethylenemethylene(9-fluorenyl)cyclopentadienylzirconium dichloride,
 isopropylene(9-fluorenyl)(1-(3-isopropyl)cyclopentadienyl)zirconium
 5 dichloride,
 isopropylene(9-fluorenyl)(1-(3-methyl)cyclopentadienyl)zirconium
 dichloride,
 diphenylmethylenemethylene(9-fluorenyl)(1-(3-methyl)cyclopentadienyl)zirconium
 dichloride,
 10 methylphenylmethylenemethylene(9-fluorenyl)(1-(3-methyl)cyclopentadienyl)-
 zirconium dichloride,
 dimethylsilyl(9-fluorenyl)(1-(3-methyl)cyclopentadienyl)zirconium dichloride,
 diphenylsilyl(9-fluorenyl)(1-(3-methyl)cyclopentadienyl)zirconium dichloride,
 diphenylmethylenemethylene(9-fluorenyl)(1-(3-tert-butyl)cyclopentadienyl)zirconium
 15 dichloride,
 isopropylene(9-fluorenyl)(1-(3-tert-butyl)cyclopentadienyl)zirconium
 dichloride,
 isopropylene(cyclopentadienyl)(1-indenyl)zirconium dichloride,
 diphenylcarbonyl(cyclopentadienyl)(1-indenyl)zirconium dichloride,
 20 dimethylsilyl(cyclopentadienyl)(1-indenyl)zirconium dichloride,
 isopropylene(methylcyclopentadienyl)(1-indenyl)zirconium dichloride,
 4-(η^5 -cyclopentadienyl)-4,7,7-trimethyl(η^5 -4,5,6,7-tetrahydroindenyl)-
 zirconium dichloride,
 [4-(η^5 -cyclopentadienyl)-4,7,7-triphenyl(η^5 -4,5,6,7-tetrahydroindenyl)]-
 25 zirconium dichloride,
 [4-(η^5 -cyclopentadienyl)-4,7-dimethyl-7-phenyl(η^5 -4,5,6,7-tetrahydro-
 indenyl)]zirconium dichloride,
 [4-(η^5 -3'-tert-butylcyclopentadienyl)-4,7,7-triphenyl(η^5 -4,5,6,7-tetra-
 hydroindenyl)]zirconium dichloride,
 30 [4-(η^5 -3'-tert-butylcyclopentadienyl)-4,7-dimethyl-7-phenyl(η^5 -4,5,6,7-tetra-
 hydroindenyl)]zirconium dichloride,
 [4-(η^5 -3'-methylcyclopentadienyl)-4,7,7-trimethyl(η^5 -4,5,6,7-tetrahydro-
 indenyl)]zirconium dichloride,
 [4-(η^5 -3'-methylcyclopentadienyl)-4,7,7-triphenyl(η^5 -4,5,6,7-tetrahydro-
 indenyl)]zirconium dichloride,
 35 [4-(η^5 -3'-methylcyclopentadienyl)-4,7-dimethyl-7-phenyl(η^5 -4,5,6,7-tetra-
 hydroindenyl)]zirconium dichloride,
 [4-(η^5 -3'-isopropylcyclopentadienyl)-4,7,7-trimethyl(η^5 -4,5,6,7-tetrahydro-
 indenyl)]zirconium dichloride,

- [4-(η^5 -3'-isopropylcyclopentadienyl)-4,7,7-triphenyl(η^5 -4,5,6,7-tetrahydroindeny)]zirconium dichloride,
 [4-(η^5 -3'-isopropylcyclopentadienyl)-4,7-dimethyl-7-phenyl(η^5 -4,5,6,7-tetrahydroindeny)]zirconium dichloride,
 5 [4-(η^5 -cyclopentadienyl)(η^5 -4,5-tetrahydropentalene)]zirconium dichloride,
 [4-(η^5 -3'-cyclopentadienyl)-4-methyl(η^5 -4,5-tetrahydropentalene)]zirconium dichloride,
 [4-(η^5 -cyclopentadienyl)-4-phenyl(η^5 -4,5-tetrahydropentalene)]zirconium dichloride,
 10 [4-(η^5 -cyclopentadienyl)-4-phenyl(η^5 -4,5-tetrahydropentalene)]zirconium dichloride,
 [4-(η^5 -3'-methylcyclopentadienyl)(η^5 -4,5-tetrahydropentalene)]zirconium dichloride,
 [4-(η^5 -3'-isopropylcyclopentadienyl)(η^5 -4,5-tetrahydropentalene)]zirconium dichloride,
 15 [4-(η^5 -3'-benzylcyclopentadienyl)(η^5 -4,5-tetrahydropentalene)]zirconium dichloride,
 [2,2,4-trimethyl-4-(η^5 -cyclopentadienyl)(η^5 -4,5-tetrahydropentalene)]-zirconium dichloride,
 20 [2,2,4-trimethyl-4-(η^5 -3,4-diisopropyl)cyclopentadienyl)(η^5 -4,5-tetrahydropentalene)]zirconium dichloride.

The preparation of the cycloolefin polymers can also be carried out in other ways which are briefly outlined below. Catalyst systems based on mixed
 25 catalysts comprising titanium salts and organoaluminum compounds are described in DD-A-109 224 and DD-A-237 070. EP-A-156 464 describes the preparation of cycloolefin polymers using catalysts based on vanadium. EP-A-283 164, EP-A-407 870, EP-A-485 893 and EP-A-503 422 describe the preparation of cycloolefin polymers using catalysts based on soluble
 30 metallocene complexes. The preparative methods and catalyst systems described in these patents for preparing cycloolefin polymers are hereby expressly incorporated by reference.

The cycloolefin polymers used according to the invention can be prepared
 35 by homopolymerization and/or copolymerization of cyclic, preferably polycyclic, olefins with retention of the rings.

The cycloolefin polymers can also be prepared by ring-opening polymerization of at least one of the monomers of the formulae I to VI and subsequent

hydrogenation of the products obtained. The cycloolefin polymers may also be prepared by ring-opening copolymerization of at least one of the monomers of the formulae I to VI with further monomers, e.g. monocyclic monomers of the formula VIII, and subsequent hydrogenation of the products obtained. The preparation of cycloolefin polymers is described in the Japanese patents JP-B-3-14882, JP-B-3-122137, JP-B-4-63807, JP-B-2-27424 and JP-B-2-276842. The preparative methods and catalyst systems described in these patents for preparing cycloolefin polymers are hereby expressly incorporated by reference. Derivatives of these cyclic olefins containing polar groups such as halogen, hydroxyl, ester, alkoxy, carboxy, cyano, amido, imido or silyl groups are likewise included.

Hydrogenated polymers and copolymers, e.g. those of styrene and dicyclopentadiene, are likewise suitable and are likewise referred to as cycloolefin polymers for the purposes of the present application.

The polymerization can also be carried out in a plurality of stages, with block copolymers also being able to be formed (DE-A-42 05 416).

Cycloolefin polymers are preferably amorphous, transparent and colorless materials. The heat distortion resistances of the cycloolefin polymers can be set within a wide range. For cycloolefin polymers, the glass transition temperature can be employed as an indication of the heat distortion resistance, as can be determined in accordance with ISO 75 part 1 and part 2 on injection-molded bodies. The cycloolefin polymers described have glass transition temperatures in the range from -50 to 220°C. Preference is given to glass transition temperatures in the range from 0 to 180°C, particularly preferably from 40 to 180°C.

The mean molar mass of the cycloolefin polymers can be controlled in a known manner by addition of hydrogen, variation of the catalyst concentration or variation of the temperature. The cycloolefin polymers present in the microstructured components according to the present invention have mass average molar masses M_w of from 1 000 to 10 000 000 g/mol. Preference is given to mass average molar masses M_w in the range from 5 000 to 5 000 000 g/mol, particularly preferably from 10 000 to 1 200 000 g/mol.

The cycloolefin polymers present in the multilayer containers of the invention have viscosity numbers in the range from 5 to 1 000 ml/g. Preference

is given to viscosity numbers in the range from 20 to 500 ml/g, particularly preferably from 30 to 300 ml/g.

- 5 The multilayer containers of the invention can also contain blends of at least one cycloolefin polymer and at least one further polymer in any mixing ratios in one or more layers.

10 For the blends with cycloolefin polymers, preference is given to using the following polymers: polyethylene, polypropylene, ethylene-propylene copolymers, polybutylene, poly(4-methyl-1-pentene), polyisoprene, polyisobutylene, natural rubber, poly(1-methyl methacrylate), further polymethacrylates, polyacrylate, acrylate-methacrylate copolymers, polystyrene, styrene-acrylonitrile copolymers, bisphenol A polycarbonate, further polycarbonates, aromatic polyester carbonates, polyethylene
15 terephthalate, polybutylene terephthalate, amorphous polyacrylate, nylon 6, nylon 66, further polyamides, polyaramides, polyether ketones, polyoxymethylene, polyoxyethylene, polyurethanes, polysulfones, polyether sulfones, polyvinylidene fluoride.

- 20 For blends of cycloolefin polymers and polyolefins, preference is given to using the following polyolefins: homopolymers of ethylene and propylene and copolymers of these two monomers, copolymers based on ethylene together with linear or branched olefins such as butene, pentene, hexene, heptene, octene, nonene, decene, undecene and dodecene, copolymers
25 based on propylene together with linear or branched olefins such as butene, pentene, hexene, heptene, octene, nonene, decene, undecene and dodecene, terpolymers of ethylene, propylene and linear or branched olefins such as butene, pentene, hexene, heptene, octene, nonene, decene, undecene and dodecene.

- 30 The blends can be produced by customary methods, e.g. by coextrusion of the polymer components from the melt, with or without use of further additives, and subsequent granulation.

- 35 Cycloolefin polymers can be processed from the melt or from solution. Suitable solvents are aprotic nonpolar hydrocarbons such as decalin or mixtures of linear or branched hydrocarbons.

The multilayer containers of the invention comprise at least one layer

- comprising at least one cycloolefin polymer together with at least one further layer of another polymer or a blend of further polymers. Suitable polymers are, for example, polyethylene, polypropylene, ethylene-propylene copolymers, polybutylene, poly(4-methyl-1-pentene), polyisoprene, polyisobutylene, natural rubber, poly(1-methyl methacrylate), further polymethacrylates, polyacrylate, acrylate-methacrylate copolymers, polystyrene, styrene-acrylonitrile copolymers, polyacrylonitrile, bisphenol A polycarbonate, further polycarbonates, aromatic polyester carbonates, polyethylene terephthalate, polybutylene terephthalate, further polyesters, amorphous polyacrylates, nylon 6, nylon 66, further polyamides, polyaramides, polyether ketones, polyoxymethylene, polyoxyethylene, polyurethanes, polysulfones, polyether sulfones, polyvinyl chloride, polyvinylidene chloride, polyvinylidene fluoride.
- 15 Particularly useful polymers are ones which have good gas barrier properties, e.g. polyesters such as polyethylene terephthalate, polyethylene naphthalate and also liquid-crystalline polyesters, polyacrylonitrile, polyvinyl chloride, polyvinylidene chloride, ethylvinyl alcohol, polyamides and others.
- 20 The production of the multilayer containers of the invention can be carried out by multicomponent injection molding, multicomponent injection blow molding and multicomponent injection stretch blow molding.
- 25 The production of preforms for multicomponent injection blow molding and multicomponent injection stretch blow molding by multicomponent injection molding leads to multilayer preforms. Multilayer preforms can be produced, for example, by coinjection of two or more materials or by injecting one or more further materials over the first layer of a material.
- 30 The production of the multilayer containers of the invention can be carried out using customary amounts of additives such as plasticizers, UV stabilizers, optical brighteners, antioxidants, antistatics, heat stabilizers or reinforcing additives such as glass fibers, carbon fibers or high-modulus fibers such as polyaramides or liquid-crystalline polyesters or the like.
- 35 Furthermore, fillers such as inorganic materials, talc, titanium dioxide or the like can be used. The abovementioned additives and fillers can have been added before the processing of the polymer materials or else can be added during processing.

It is possible to join the various polymer layers to one another by use of bonding layers. Materials suitable for this purpose are, for example, polyolefins such as the materials Tafmer[®], Admer[®] from Mitsui Chemicals.

5 However, it has surprisingly been found that the cycloolefin polymers used according to the invention display excellent adhesion to the other layers. Use of bonding layers can therefore be dispensed with, which is of great economic advantage owing to the lower material costs and the greater simplicity of the production of the multilayer containers.

10 The cycloolefin copolymers used according to the invention surprisingly display a significant improvement in the mechanical properties in the production of multilayer systems according to the invention without bonding layers.

15 The adhesion between the various layers of the multilayer containers of the invention can be optimized by matching the shrinkage behavior of the different materials used according to the invention.

20 Compared to containers produced from only cycloolefin polymers, the multilayer containers of the invention have improved resistance to impacts and also display improved resistance to oils and fats.

25 Due to their high purity, extraordinarily low water absorption, excellent barrier properties toward gases and moisture, their good blood compatibility, excellent biocompatibility, good sterilizability by means of hot steam, hot air, ethylene oxide gas and high-energy radiation (gamma-rays and electron beams), high resistance to acids, alkalis and polar solvents, the multilayer containers of the invention are very suitable for packaging
30 and storage in the medical, pharmaceutical, cosmetic and food sectors, e.g. in the form of syringes, injectors, cartridges, vials and bottles, tubes and other containers.

35 Owing to their particular properties, the multilayer containers of the invention are extremely well suited to hot packaging of liquids in these containers, e.g. in the food sector.

The invention is illustrated by the following examples.

Examples

Example 1 - 2-component injection molding

5

Inlay injection molding of Topas on a tensile bar tool having two cavities

10 The experiments were carried out using a Krauss Maffei model KM 90-210B injection molding machine and a tool for producing DIN standard tensile bars having two cavities in an S shape.

15 To prepare for the experiments, tensile bars were produced from all materials and were halved. The part of the tensile bar farthest from the gate was used as inlay for the 2-component injection molding procedure. For this purpose, the halved tensile bar (inlay) was placed in the tool in its original position and the missing half of the tensile bar was in each case injected onto it using the second polymer (over-injected polymer; see table 1). Tensile tests were then carried out on the resulting tensile bars with joining seam in accordance with ISO 527-1 to determine the rupture stress and elongation at break (see table 1).

20

The processing conditions are shown in tables 2 and 3.

25

Table 1

Over-injected polymer	Test specimen initially placed in the tool	Rupture stress	Elongation at break
		(MPa)	(%)
LLDPE Innovex	Topas 6013 Lot 74093	3.9	11.8
Hostalen PPR 1042	Topas 6013 Lot 74093	3.7	3.6
Impet PET TS6	Topas 6013 Lot 74093	8.3	4.4
Nylon MXD6	Topas 6013 Lot 74093	-	-
Bayer PC CD 2005	Topas 6013 Lot 74093	-	-
DSM Stanylan LDPE-	Topas 8007 Lot 54028	2.4	8.1
Hostalen PPR 1042	Topas 8007 Lot 54028	9.2	7.0
Impet PET T86	Topas 8007 Lot 54028	8.7	5.3
Nylon MXD6	Topas 8007 Lot 54028	990	6.3
Bayer PC CD 2005	Topas 8007 Lot 54028	-	-
Topas 6013 Lot 74093	DSM Stanylan LDPE	6.8	53.1
Topas 6013 Lot 74093	Hostalen PPR 1042	1.0	0.85
Topas 6013 Lot 74093	Impet PET T86	3.3	2.6
Topas 6013 Lot 74093	Nylon MXD6	3.7	2.7
Topas 6013 Lot 74093	Bayer PC CD 2005	-	-
Topas 8007 Lot 54028	DSM Stanylan LDPE	4.4	16.9
Topas 8007 Lot 54028	Hostalen PPR 1042	8.5	6.6
Topas 8007 Lot 54028	Impet PET T86	4.8	3.3
Topas 8007 Lot 54028	Nylon MXD6	5.0	3.2
Topas 8007 Lot 54028	Bayer PC CD 2005	6.0	3.9

- 15 -

Table 2: Injection molding conditions:

Over-injected polymer	Test specimen initially placed in the tool	Melt temp. (°C)	Mold temp. (°C)	Back pressure (bar)*	Rotational speed of screw (rpm)**	Plasticizing stroke (mm)	Injection rate (%)***	Hold pressure time (bar)* / (sec)	Injection pressure (bar)*	Cooling time (sec)	Melt cushion (mm)
LLDPE Innovex	Topas 6013 Lot	210	35	12	50	63	100	~ 43/15		> 60	~ 5
Hostalen PPR	Topas 6013 Lot	230	50	12	50	63	100	43/15	46	> 60	~ 4
Impet PET T86	Topas 6013 Lot	270	60	12	50	60	100	23/10	51	> 50	
Nylon MXD6	Topas 6013 Lot	270	45-30	12	50	49	100	18/10	37	> 50	
Bayer PC CD	Topas 6013 Lot	280	30-120	12	50	55	100	3/10	29	> 40	
Grilamid TR 90	Topas 6013 Lot	275	35	13	50	52	100	8/10	30	> 50	~ 6
DSM Stanylan	Topas 8007 Lot	210	35	13	50	61	100	35/15	40	> 60	~ 5
Hostalen PPR	Topas 8007 Lot	230	50	13	50	60	100	33/15	36	> 60	~ 5
Impet PET T86	Topas 8007 Lot	275	45	13	50	55	100	8/10	49	> 60	5
Nylon MXD6	Topas 8007 Lot	275	35	13	50	53	100	8/10	34	> 60	5
Bayer PC CD	Topas 8007 Lot	280	40-20	13	50		100			> 60	~ 4
Grilamid TR 90	Topas 8007 Lot	275	35	13	50	55	100	8/10	33	> 50	~ 5

* Pressures are hydraulic pressures

** 50% ~ 180 rpm

*** 100% ~ 200 mm/sec.

Table 3: Injection molding conditions:

Over-injected polymer	Test specimen initially placed in the tool	Melt temp. (°C)	Mold temp. (°C)	Back pressure (bar)*	Rotational speed of screw (%)**	Plasticizing stroke (mm)	Injection rate (%)***	Hold pressure time (bar)* / (sec)	Injection pressure (bar)*	Cooling time (sec)	Melt cushion (mm)
Topas 6013 Lot 74093	DSM Stanylan LDPE	270-260	35	13	50	54	100	13/10	41	> 50	5
Topas 6013 Lot 74093	Hostalen PPR 1042	270-260	40	13	50	54	100	8/10	47	> 50	5
Topas 6013 Lot 74093	Impet PET T86	270-260	100	13	50	54	100	8/10	47	> 50	6
Topas 6013 Lot 74093	Nylon MXD6	270-260	100	13	50	54	100	8/10	53	> 50	6
Topas 6013 Lot 74093	Bayer PC CD 2005	270-260	60-110	13	50		100			> 50	6
Topas 6013 Lot 74093	Grilamid TR 90	270-260	110	13	50	51	100	8/10	52	> 50	- 4
Topas 8007 Lot 54028	DSM Stanylan LDPE	230-220	35	13	50	54	100	13/10	34	> 50	4
Topas 8007 Lot 54028	Hostalen PPR 1042	230-220	40	13	50	54	100	13/10	33	> 50	4
Topas 8007 Lot 54028	Impet PET T86	230-220	40	13	50	54	100	13/10	34	> 50	5
Topas 8007 Lot 54028	Nylon MXD6	230-220	40	13	50	54	100	13/10	33	> 50	5
Topas 8007 Lot 54028	Bayer PC CD 2005	230-220	40	13	50	54	100	13/10	34	> 50	4.5
Topas 8007 Lot 74054	Grilamid TR 90	220-230	40	13	50	54	100	8/10	29	> 50	- 4

* Pressures are hydraulic pressures

** 50% ~ 180 rpm

*** 100% ~ 200 mm/sec.

- 17 -

Example 2 - 2-component injection molding

Coinjection of Topas by injection molding using a multi-part mold

5 This was carried out using a 3-component Klöckner Ferromatik injection molding machine and a centrally gated plate ($300 \times 215 \times 3$ mm).

10 Using a special injection head having controlled and sprung needle valves, the injection head nozzle was selected by means of a preceding 2-component distributor disk so that the core component was injected centrally into the cavity and the second melt exiting coaxially around it was injected simultaneously or, if desired, after an interval (see fig. 1).

15 Mixing of the two streams of material was avoided by selection of the respective fluidities and, in particular, by selection of the injection sequence/process conditions.

20 Formation of the core layer, here component B, was monitored in the case of transparent or slightly colored materials. As colorant, a Topas 5013 (cycloolefin copolymer/Ticona; HDT/B (0.45 N/mm^2) = 130°C ; melt index MVR at 260°C , $2.16 \text{ kg} = 56 \text{ ml/min}$)/Sandoplast Blau B masterbatch was added in a concentration of about 2%.

Selection of the component A of the outer layer and the component B of the core layer is summarized in table 4.

Table 4: Material combinations:

Component B		Component A	
Topas 8007	Cycloolefin copolymer/Ticona HDT/B (0.45 N/mm^2) = 75°C melt index MVR at 260°C , 2.16 kg = 30 ml/min	Metocen PP X50081 94-2710/Tagor	Transparent polypropylene
Topas 8007	Cycloolefin copolymer/Ticona HDT/B (0.45 N/mm^2) = 75°C melt index MVR at 260°C , 2.16 kg = 30 ml/min	K-Resin KR-01/ Phillips	Styrene- butadiene copolymer
Topas 6013	Cycloolefin copolymer/Ticona HDT/B (0.45 N/mm^2) = 130°C melt index MVR at 260°C , 2.16 kg = 13 ml/min	PET Polyester T86 W03/Kosa	Transparent polyester
Topas 6013	Cycloolefin copolymer/Ticona HDT/B (0.45 N/mm^2) = 130°C melt index MVR at 260°C , 2.16 kg = 13 ml/min	Grilamid TR90/ EMS-Chemie	Transparent polyamide
Topas 6013	Cycloolefin copolymer/Ticona HDT/B (0.45 N/mm^2) = 130°C melt index MVR at 260°C , 2.16 kg = 13 ml/min	Nylon MXD 6/Mitsui	Transparent polyamide
Topas 6013	Cycloolefin copolymer/Ticona HDT/B (0.45 N/mm^2) = 130°C melt index MVR at 260°C , 2.16 kg = 13 ml/min	Trogamid CX7323/ Degussa-Höls	Transparent polyamide
Topas 6013	Cycloolefin copolymer/Ticona HDT/B (0.45 N/mm^2) = 130°C melt index MVR at 260°C , 2.16 kg = 13 ml/min	Metocen PP X50081 94-2710/Tagor	Transparent polypropylene

Procedure:

- The various material combinations were each processed for two different injection profiles. The profiles differed in the sequence of injection of the enveloping component (component A) and the core component (component B).

Example 2a:

5 In the case of injection profile 2a, the time delay between commencement of injection of the component B and the component A was about two seconds, at which time 82 percent of the amount of component A had already been injected. The injection profile 2a is shown by way of example in fig. 2a for polyester/Topas 6013.

Example 2b:

10 In the case of the injection profile 2b, the time delay between commencement of injection of component B and component A was only about 0.5 seconds. After this time, about 90 percent of the remaining amounts were injected simultaneously. The injection profile 2b is shown by way of example in fig. 2b for Trogamid/Topas 6013.

15 In both cases, the sprue is sealed with the component A at the end of the respective injection procedure. Further processing parameters for the experiments are shown in table 6.

20 Breakthrough of the enveloping layer through the core component was not observed, even when using very fluid enveloping material such as Metocen PP X50081.

The layer thickness distribution can be influenced via the respective injection volumes, injection pressures and injection rates of the 2 independently regulatable injection molding units, while the position of the core layer can be shifted by means
25 of the temperature of the tool.

Uniform layer thickness distributions and good transparency of the plates can be achieved under the above-described process conditions. In addition, the plates were assessed in respect of adhesion of the layers and distortion tendency (see table 5).

Table 5: Experimental results:

Injection molding profile	Material combination Component A/ Component B	Adhesion between layers	Clouding	Distortion tendency
2a I	Metocen PP / Topas 8007	++	0	-
2b I	Metocen PP / Topas 8007	++	+0	-
2a II	K-Resin / Topas 8007	+	+0	+0
2b II	K-Resin / Topas 8007	+	+	+0
2a III	Metocen PP / Topas 6013	+	0	-
2b III	Metocen PP / Topas 6013	+	+0	-
2a IV	Trogamid / Topas 6013	+0	+	+0
2b IV	Trogamid / Topas 6013	+0	++	+0
2a V	Grilamid / Topas 6013	0	+	+
2b V	Grilamid / Topas 6013	0	+	+
2a VI	PET Polyester / Topas 6013	-	0-	+
2b VI	PET Polyester / Topas 6013	-	0	+
2a VII	Nylon MXD6 / Topas 6013	0-	0-	+
2b VII	Nylon MXD6 / Topas 6013	0-	0	+

Table 6: Processing parameters:

[illegible]

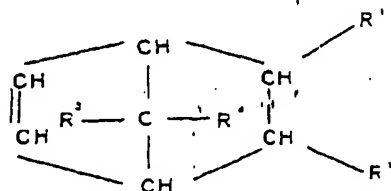
WO/00/61370

- 23 -

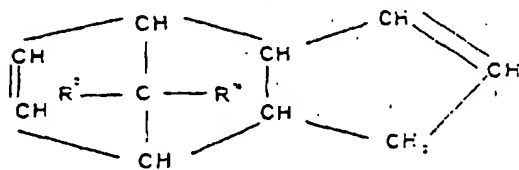
PCT/EP00/02666

Claims

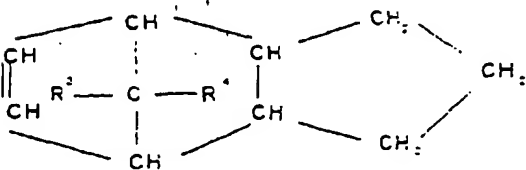
1. A multilayer container comprising at least one layer which comprises at least one cycloolefin polymer.
2. A multilayer container as claimed in claim 1 comprising at least one layer which comprises at least one cycloolefin polymer comprising 0.1-100% by weight, based on the total mass of the cycloolefin polymer, of polymerized units derived from at least one polycyclic olefin of the formula I, II, II', III, IV, V or VI



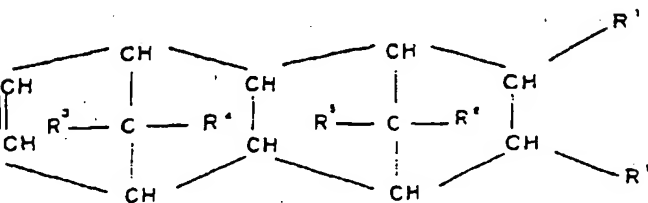
(I),



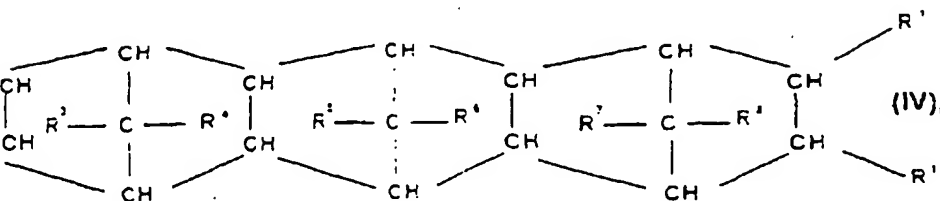
(II),



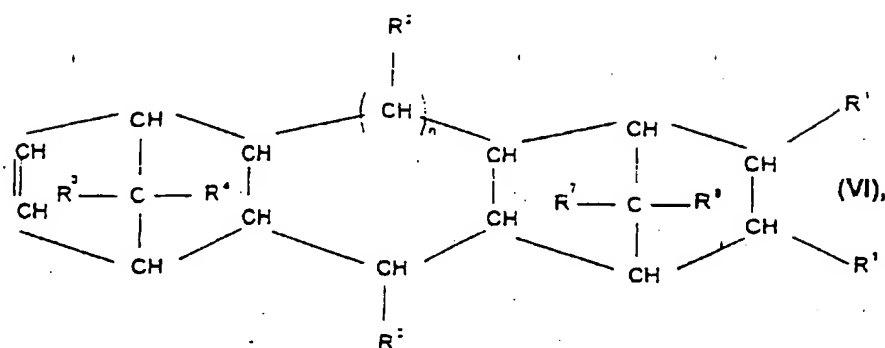
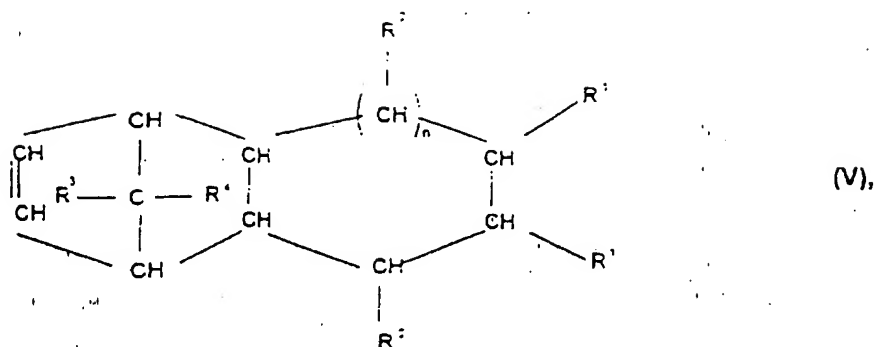
(II'),



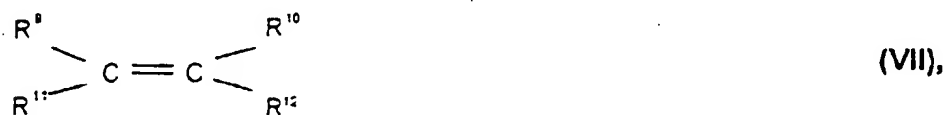
(III),



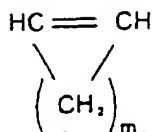
(IV),



where $R^1, R^2, R^3, R^4, R^5, R^6, R^7$ and R^8 are identical or different and are each a hydrogen atom or a C₁-C₂₀-hydrocarbon radical such as a linear or branched C₁-C₈-alkyl radical, C₆-C₁₈-aryl radical, C₇-C₂₀-alkylenaryl radical, a cyclic or acyclic C₂-C₂₀-alkenyl radical or form a saturated, unsaturated or aromatic ring, where identical radicals R^1 to R^8 in the various formulae I to VI may have different meanings and n is from 0 to 5, and from 0 to 99.9% by weight, based on the total mass of the cycloolefin polymer, of polymerized units derived from one or more acyclic olefins of the formula VII



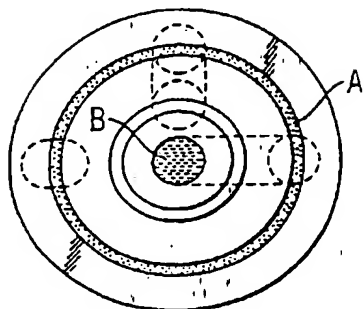
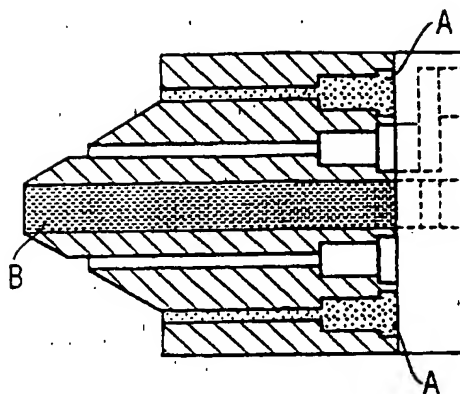
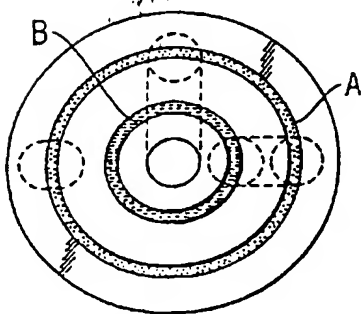
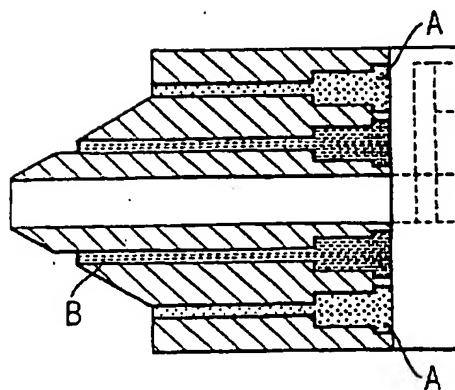
where R^9, R^{10}, R^{11} and R^{12} are identical or different and are each a hydrogen atom or a linear, branched, saturated or unsaturated C₁-C₂₀-hydrocarbon radical such as a C₁-C₈-alkyl radical or a C₆-C₁₈-aryl radical, and from 0 to 45% by weight, based on the total composition of the cycloolefin polymer, of polymerized units derived from one or more monocyclic olefins of the formula VIII



(VIII),

where m is from 2 to 10.

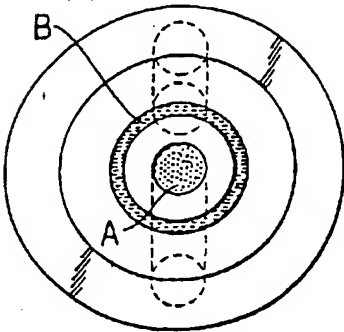
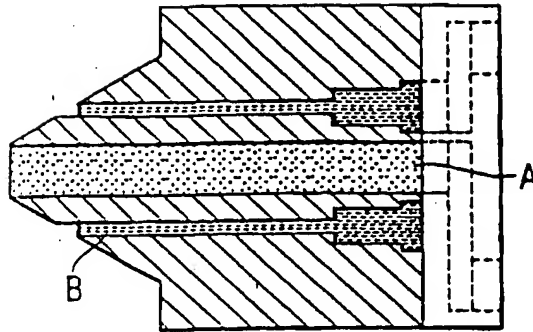
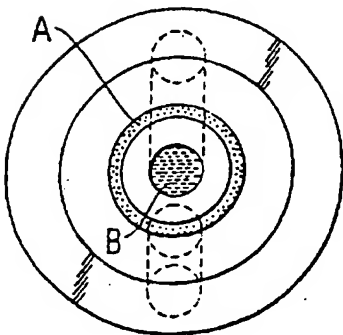
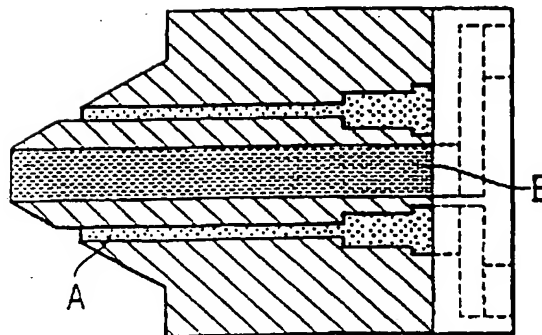
3. A process for producing a multilayer container as claimed in claim 1 or 2, wherein the multilayer container is produced by multicomponent injection molding, multicomponent injection blow molding or multicomponent injection stretch blow molding.
4. A preform for producing a multilayer container as claimed in claim 1 or 2 obtainable by coinjection of two or more materials or by injecting at least one further material over the first layer of a material.
5. The use of a multilayer container as claimed in claim 1 or 2 for packaging in the medical, pharmaceutical, cosmetic or food sector.
6. The use of a multilayer container as claimed in claim 1 or 2 for hot packaging of liquids.

Fig. 1b**Fig. 1a****Fig. 2b****Fig. 2a**

WO 00/61370

PCT/EP00/02666

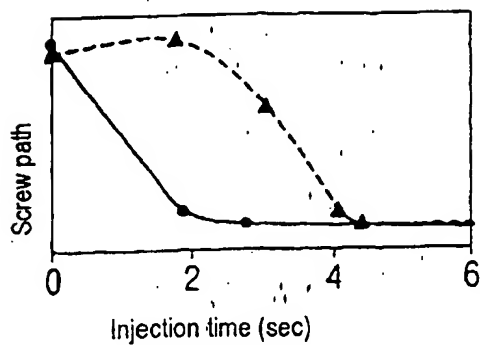
2/3

Fig. 3b**Fig. 3a****Fig. 4b****Fig. 4a**

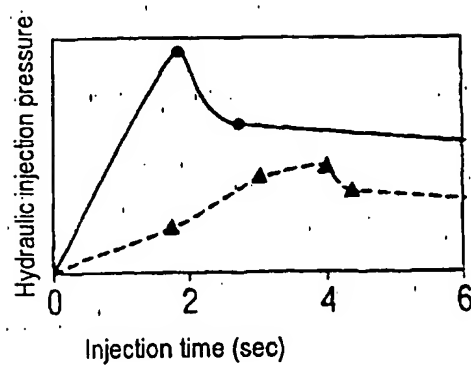
WO 00/61370

PCT/EP00/02666

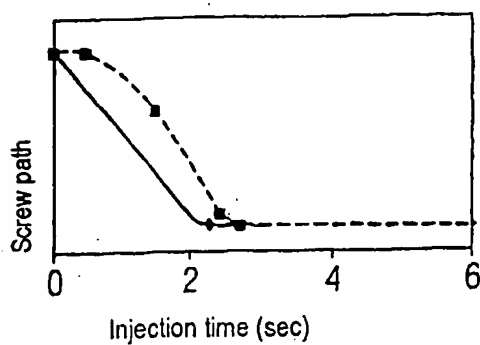
3 / 3

Fig. 5a

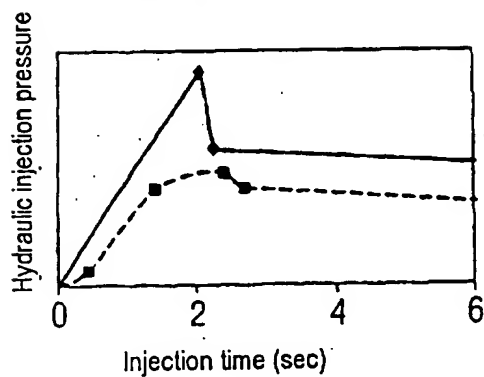
—●— A (Polyester)
-▲- B (Topas 6013)

Fig. 5b

—●— A (Polyester)
-▲- B (Topas 6013)

Fig. 6a

—●— A (Trogamid)
-▲- B (Topas 6013)

Fig. 6b

—●— A (Trogamid)
-▲- B (Topas 6013)

